

The Thermal Decomposition of Mixtures of Some Anhydrous Metallic Sulfates

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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Robert Dudley Fowler
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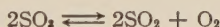
THE THERMAL DECOMPOSITION OF MIXTURES OF SOME ANHYDROUS METALLIC SULFATES

Introduction

When heated to high temperatures, the metal sulfates are reversibly decomposed into sulfur trioxide and oxides. The decomposition may take place in one of several ways, depending on the particular metal. In some cases decomposition results directly in an oxide wherein the metal has the same valence as in the sulfate; other sulfates decompose in steps, a basic sulfate first being formed, which subsequently decomposes into the oxide; in the decomposition of other sulfates, the metal may be oxidized or reduced. The sulfates which have been studied may be classified as follows

Type 1	$\text{MSO}_4 \rightleftharpoons \text{MO} + \text{SO}_3$	$\text{NiSO}_4, \text{CoSO}_4, \text{MgSO}_4$
Type 2	$x\text{MSO}_4 \rightleftharpoons x\text{MO} \cdot \text{SO}_3 + (x-1)\text{SO}_3$	$\text{ZnSO}_4, \text{CuSO}_4, \text{CdSO}_4, \text{BeSO}_4$
Type 3	$\text{M}_2(\text{SO}_4)_3 \rightleftharpoons \text{M}_2\text{O}_3 + 3\text{SO}_3$	$\text{Fe}_2(\text{SO}_4)_3, \text{Al}_2(\text{SO}_4)_3, \text{Ga}_2(\text{SO}_4)_3$
Type 4	$x\text{M}_2(\text{SO}_4)_3 \rightleftharpoons x\text{M}_2\text{O}_3 \cdot \text{SO}_3 + (x-1)\text{SO}_3$	$\text{Cr}_2(\text{SO}_4)_3$ rare earth sulfates
Type 5	$\text{M}(\text{SO}_4)_2 \rightleftharpoons \text{MO}_2 + 2\text{SO}_3$	$\text{Th}(\text{SO}_4)_2$
Type 6	$4\text{M}(\text{SO}_4)_2 \rightleftharpoons 2\text{M}_2(\text{SO}_4)_3 + 2\text{SO}_3 + \text{O}_2$	$\text{Ce}(\text{SO}_4)_2$
Type 7	$\text{M}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{MO}_2 + 2\text{SO}_3 + \text{SO}_2$	$\text{Ce}_2(\text{SO}_4)_3$
Type 8	$2\text{MSO}_4 \rightleftharpoons \text{M}_2\text{O}_3 + \text{SO}_3 + \text{SO}_2$	FeSO_4
Type 9	$3\text{MSO}_4 \rightleftharpoons \text{M}_3\text{O}_4 + 2\text{SO}_3 + \text{SO}_2$	MnSO_4
Type 10	$2\text{M}_2\text{SO}_4 \rightleftharpoons 4\text{M} + 2\text{SO}_3 + \text{O}_2$	Ag_2SO_4
Type 11	$\text{MSO}_4 \cdot \text{K}_2\text{SO}_4 \rightleftharpoons \text{K}_2\text{SO}_4 + \text{MO} + \text{SO}_3$	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4, \text{BeSO}_4 \cdot \text{K}_2\text{SO}_4$

In each case there is also a second, simultaneous reaction, the reversible dissociation of SO_3 into SO_2 and O_2



The earlier investigators¹ were mainly interested in metallurgical processes involving the roasting of sulfates, and their work consisted in determining the temperatures at which dissociation began to be appreciable.

Measurements of the dissociation pressures of the sulfates of the commoner elements have been made by Keppeler and d'Ans,² Wöhler, Plüddemann, and Wöhler,³ and Marchal⁴ and of some rare earth sulfates by

¹ Boussingault, *Ann. de Chimie* [4] **12**, 419 (1867); Kerl, "Grundriss der Metallhüttenkunde," Leipzig, **1881**, p. 70; Ditte, "Étude générale des Sels," Paris, **1906**; Bradford, *Trans. Am. Inst. Min. Eng.*, **33**, 50 (1903); Friedrich and Blickle, *Metallurgie*, **7**, 323 (1910), and *Stahl u. Eisen*, **31** (1909); Landis, *Met. and Chem. Eng.*, **VIII**, No. 1, 22; Warlimont, *Metallurgie*, **6**, 130 (1903); Hofman, *Trans. Am. Inst. Min. Eng.*, **35**, 812 (1905), and *ibid.*, **39**, 628 (1909); Mostowitsch and Doeltz, *Zeit. f. anorg. Chemie*, **54**, 146 (1907), and *Metallurgie*, **6**, 450 (1909); Barth, *Metallurgie*, **9**, 199 (1912); Hofman and Wanjukow, *Trans. Am. Inst. Min. Eng.*, **43**, 523 (1913).

² Keppeler and d'Ans, *Z. physik. Chem.*, **62**, 89 (1908).

³ Wöhler, Plüddemann and Wöhler, *Ber.*, **31**, 703 (1908).

⁴ Marchal, *J. chim. phys.*, **22**, 325, 412, 493, 559 (1912).

Wöhler and Grünzweig.⁵ The dissociation pressure curves of some of the commoner elements are given in Fig. 1. The curves for the rare earths are given in Reference 5. It will be seen from these curves, that the pressures for different sulfates at any given temperature vary considerably, depending on the nature of the metal.

In the case of the double sulfates $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$ and $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4$, the dissociation pressures are not those of MgSO_4 and BeSO_4 at the same

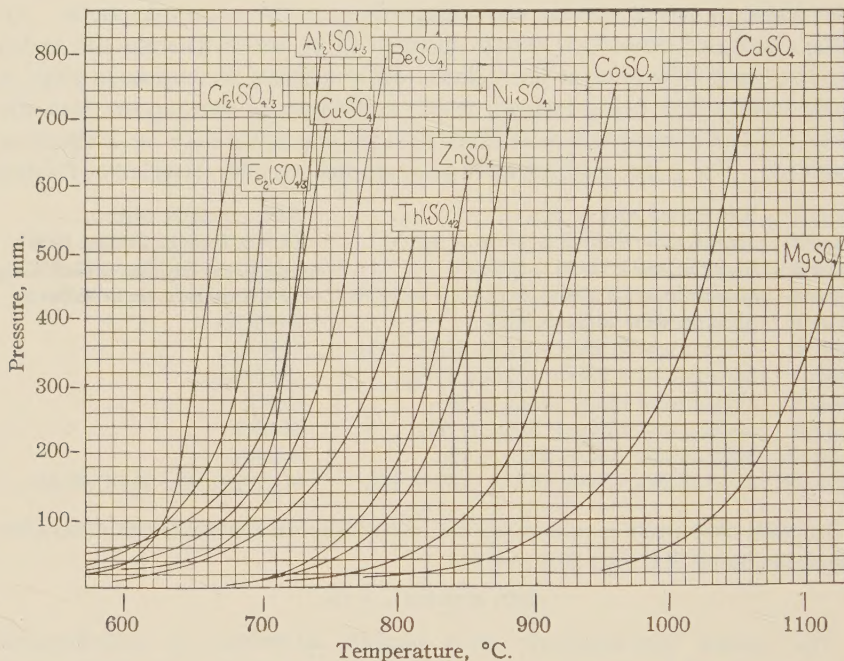


Fig. 1.—Dissociation pressures of some anhydrous sulfates.

temperatures, but are considerably lower. With mixtures of ZnSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ the pressure is that of $\text{Fe}_2(\text{SO}_4)_3$, the less stable of the two. No other double salts or mixtures are reported in the literature as having been studied.

The solid decomposition product of any one of the sulfates listed is insoluble in water. Consequently, if a mixture of two sulfates were heated to some definite temperature, and the pressure of the gas phase maintained above the equilibrium pressure of the first sulfate, and below that of the second, the first would remain unaltered, while the second would form the insoluble product of decomposition. If the mixture could then be cooled before the reaction reversed appreciably, and then leached with water, the unaltered sulfate would be dissolved, thus removing it from the mixture.

⁵ Wöhler and Grünzweig, *Ber.*, **46**, 1726 (1913).

In this manner the otherwise very difficult separation of such elements as nickel and cobalt, beryllium and aluminum, hafnium and zirconium and particularly the metals of the rare earths, might be comparatively easily effected.

Both Wöhler and Grünzweig, and Mlle. Marchal call attention to the possibility of such separations; they considered them entirely feasible. Wöhler and Grünzweig carried out the controlled decomposition of neodymium sulfate at such temperature and pressure that praseodymium sulfate placed next to it remained unchanged. They considered this a sufficient proof that separations were possible; no attempts at the actual separations of the mixtures have been described.

For the accomplishment of such separations, three factors are essential: (1) the sulfates must exert the same dissociation pressures in mixtures as they do individually; (2) the rate of the reverse reaction must be sufficiently slow to allow "quenching" of the equilibrium; and (3) the maintaining of the sulfates at high temperatures must not so change the physical state of the unaltered sulfate that its solution in water is made difficult.

The behavior of mixtures of sulfates on heating is of further interest, in connection with the study of solid solutions, which has been limited until comparatively recently to metals and a few chlorides. There have been several methods used in the study of solid solutions in metals such as the study of melting and freezing point diagrams, temperature-resistance curves, temperature-thermoelectric force curves, and determination of the crystal lattice constants from x-ray measurements. With solid solutions of salts, however, only the melting or freezing point method, and the use of x-rays, can be employed. Sulfate mixtures cannot, in general, be studied by the melting and freezing point method, since, for the most part, they decompose on heating, before melting. If two sulfates are miscible, it is very likely that their dissociation pressures will be considerably altered, and a study of their thermal decomposition at definite temperatures and pressures should be of interest in connection with the study of solid solutions.

The purpose of this research was to study the thermal decomposition of metal sulfates, with the objectives: (1) to determine the nature of the dissociation of, and (2) to ascertain the comparative structures of (*a*) mixtures of non-isomorphous sulfates, (*b*) mixtures of isomorphous sulfates; (*c*) double sulfates; (3) to determine the feasibility of the separation of elements by the controlled decomposition of mixtures of their anhydrous sulfates.

Apparatus

The construction of the furnace used to decompose the sulfates at high temperatures is readily seen from Fig. 2. The major portion of the heat was supplied by a No. 16 B. and S. gage chromel ribbon *a*, 13 mm. in width, wound into a helix 48 mm. in diameter, with 3 mm. spacing between the turns. This was encased by an alundum

tube b, 60 cm. long, having an internal diameter of 50 mm. and a wall thickness of 5 mm. The ends of the ribbon were bent at right angles to the axis of the helix, and brought out to heavy brass clamps, c, c', through slots in the ends of the alundum tube.

To compensate for radiation loss at the ends of the furnace, coils d, d', of No. 6 B. and S. gage chromel wire were wound around the outside of the alundum tube, 5 cm. from each end. Each coil consisted of seven turns, with 10 mm. spacing. The two coils were connected in series, and the ends brought out through the furnace ends to the brass clamps e, e'.

A 25-cm. steel cylinder, A, 57 cm. long, formed the outer jacket of the furnace. Transite disks g, g', 16 mm. thick at each end of the jacket, served to support the alundum tube and heating coils so that their axes and the axis of the jacket were coincident. The space between the alundum tube and the inner wall of the jacket was filled with Filter-cel, which proved a satisfactory heat insulator. The furnace was horizontally

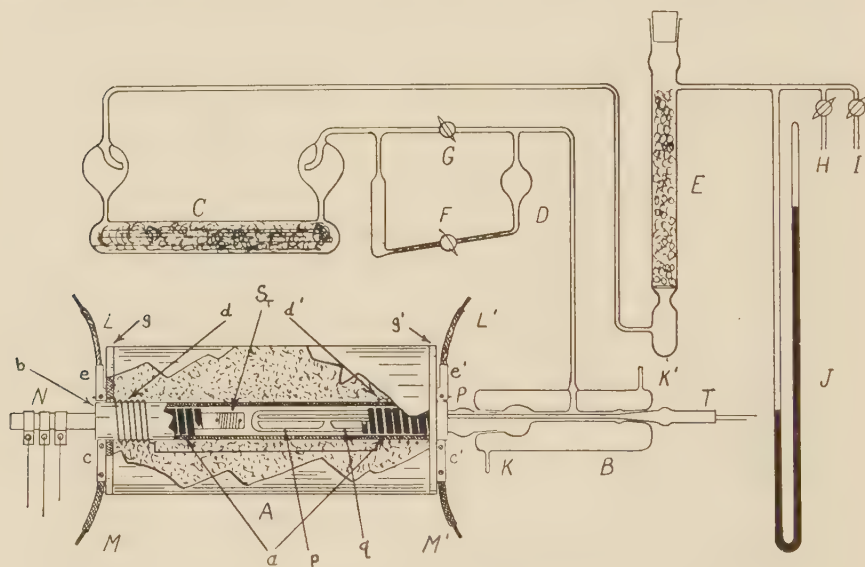


Fig. 2.—Apparatus for the controlled thermal decomposition of anhydrous metal sulfate mixtures.

suspended between parallel steel rods, which served as runners upon which to slide it into position over the reaction tube.

The main and end coils were heated separately by currents of 40–60 amperes at 10–15 volts, supplied through transformers. Since it was not practicable to adjust the heavy secondary currents by resistance variation, adjustment was made by varying the low current in the primary circuit, and as the currents in the main and end coils had to be adjusted independently, the use of two transformers was necessary.

The temperature of the furnace was automatically maintained constant, using the temperature variation in resistance of a small coil of fine platinum wire inside the furnace as a means of keeping the heating currents at definite average values. Reference to Fig. 3 will aid in the description of the operation. The platinum coil S_r having a resistance of about 50 ohms at 1000°, together with the 50-ohm constantan resistances S_1 and S_2 , and the variable constantan resistance S_3 , form a Wheatstone bridge, to which

current is supplied by the six-volt storage battery B. Resistance S_3 is set equal to the value that the thermostat coil S_T is to have at the desired furnace temperature. If the furnace is at this temperature the Wheatstone bridge is balanced, and no current flows through the galvanometer G. When these conditions prevail, light falling from a source L, through a lens O, onto the galvanometer mirror, just misses being reflected to a focus on the photo-electric cell P. However if the furnace temperature falls below the desired value, the resistance of S_T decreases and the bridge becomes unbalanced. This causes the reflection of the beam of light onto the photo-electric cell, bringing about a current flow through the latter. The photoelectric current is multiplied by the thermionic amplifier A to a value large enough to close the switch N, thereby decreasing the resistances in the primary circuits of the transformers T_1 and T_2 . The IR drop across each primary is thus increased, with a consequent attendant increase in the secondary currents through the main coil M, and the end coils E, E', resulting in a rise in the tem-

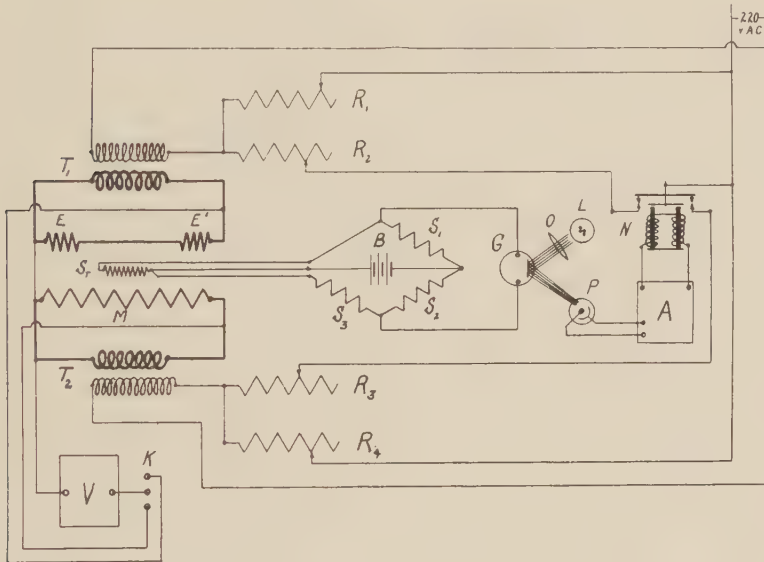


Fig. 3.—Circuit for furnace control.

perature of the furnace. When the desired temperature has again been reached, S_T has a resistance equal to that of S_3 , and the bridge is balanced, and the beam of light no longer falls on the photo-electric cell, allowing the switch N to open. The values of R_1 and R_4 are such that the secondary currents are now insufficient to maintain the furnace at the desired temperature, so that it again cools, repeating the cycle. In this manner, the temperature of the furnace fluctuates through a small interval, with the desired temperature as the average value.

The IR drop across the heating coils was measured with the voltmeter V, which could be thrown across the desired coil by means of the switch K. In this way the optimum secondary voltages of T_1 and T_2 were determined for a series of temperatures at 50-degree intervals, over the range to 1050° , thus allowing the furnace to be subsequently maintained at any desired temperature within this range with the minimum expenditure of time and labor. Thus, if it were desired to maintain the furnace at 1000° , R_3 and R_4 were so adjusted that the IR drop across the main heating coil fluctuated

between 9 and 13 volts, while R_1 and R_2 were given such values that the potential across the end coils varied between 8.5 and 11.5 volts. R_1 and R_4 each consisted of two series-connected, 37-ohm, water-cooled rheostats, and R_2 and R_3 were single 37-ohm rheostats of the same type.

The galvanometer G was a Leeds and Northrup Type R, having a sensitivity of 250 megohms.

The photo-electric cell was of the potassium hydride type, and was illuminated

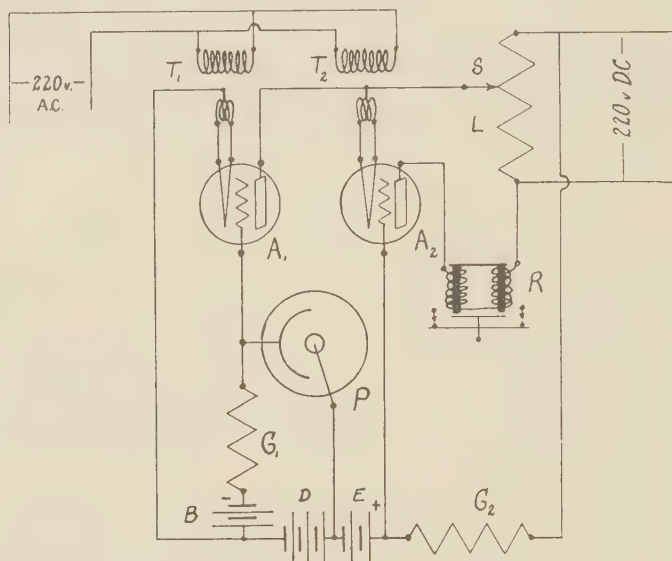


Fig. 4.—Amplifier circuit: A_1 and A_2 , Western Electric 216A power amplifiers; T_1 and T_2 , 220 to 5.5 volt transformers; P , photo-electric cell; G_1 , 15 megohm grid leak; G_2 , 0.1 megohm grid leak; B , 45-volt battery; D , 67.5-volt battery; E , 112.5-volt battery; L , 1400-ohm slide wire rheostat; R , 2600-ohm magnetic switch.

by a 27-candle-power, 6-volt lamp. Under the conditions of the present arrangement, full illumination of the photo-electric cell produced a current of about 3×10^{-7} amperes, when a potential of 112.5 volts was applied to it. This small current was boosted by thermionic amplification to about 30 milli-amperes, which nicely operated the switch changing the furnace current. The amplifier circuit is shown in Fig. 4. As the principles and applications of thermionic amplification have been thoroughly discussed by Van der Bijl,⁶ Morecroft,⁷ Nottingham,⁸ and others, the circuit will not be described here.

In connecting the platinum resistance S_r to the other arms of the Wheatstone bridge, the three lead method of Siemens⁹ was used to compensate for any variation in

⁶ Van der Bijl, "The Thermionic Vacuum Tube," McGraw-Hill Book Co., Inc., New York, 1920.

⁷ Morecroft, "Principles of Radio Communication," John Wiley and Sons, Inc., New York, 1921.

⁸ Nottingham, *J. Franklin Instit.*, 208, 469 (1929); 209, 287 (1930).

⁹ Burgess and le Chatelier, "The Measurement of High Temperatures," John Wiley and Sons, Inc., New York, 1912.

the resistance of the flexible copper wire leads that might be brought about by changes in the temperature of the room.

This thermostat served to maintain the furnace constant to within 0.1° , for as long as twenty-four hours. By properly supplementing the heat supplied by the main furnace coil with that from the end coils, the temperature could be maintained uniform to within 1° , over a central portion of the furnace extending to about 10 cm. from each end.

Temperature Measurement.—Temperature measurement was made by a platinum-platinum-rhodium thermocouple, placed inside the reaction chamber. The cold junction was immersed in a mixture of ice and water in a Dewar flask. A Leeds and Northrup thermocouple potentiometer and a Leeds and Northrup Type R galvanometer having a sensitivity of 250 megohms were used in conjunction with the thermocouple. The Holman formula

$$\log e = n \log t + \log m$$

was used to convert the e. m. f. values of the thermocouple to temperatures (see reference 9, page 112). Temperatures of fixed points determined by using this formula have a maximum departure of -2.5° from the gas thermometer scale values. The values of the temperature and pressure of sulfur trioxide were so chosen for each pair of sulfates that such a departure would have no effect. In the case of the sulfates of praseodymium and neodymium, where the difference in dissociation pressures is the smallest of all the pairs studied, the pressures of sulfur trioxide at 1015° are, respectively, 715 and 780 mm., and at 1017.5° , 740 and 810 mm. Consequently, a positive error of 2.5° in setting the temperature is just permissible. With all the other sulfate pairs, a greater error is permissible. To determine the constants n and m , the e. m. f.'s of the thermocouple were measured at the sulfur boiling point, and at the melting point of gold, the latter point being obtained by the wire method (reference 9, page 183–185). At 1000° , the thermo-electric power, dE/dt , of the thermocouple was 11.5 microvolts per degree, consequently a change of temperature of 0.1° would produce an e. m. f. change of 1.15 microvolts, which is well within the sensitivity of the potentiometer. It is probable that the control apparatus could be eliminated by the use of a source of power of constant voltage, such as would be obtained by the use of a suitable voltage regulator, or from a generator driven by a synchronous motor.

Decomposition Chamber and Constant Pressure System.—The arrangement of the decomposition apparatus is shown in Fig. 2. The sulfate mixture to be investigated was placed in a porcelain boat *p*, in the quartz tube *P*. This quartz tube was ground into the Pyrex jacket *B*, through which water at 70 – 80° was circulated, by means of an electric heater and reservoir forming a closed hydraulic circuit through connections at *K* and *K'*. The thermocouple was encased in a quartz tube *T*, ground into the other end of the jacket. This jacket served to keep the ground joints cool and, simultaneously, to prevent the condensation of sulfur trioxide. A T-connection led from the interior through the side of the jacket, to the phosphoric acid by-pass *D*, which was connected in turn to the manometer *J*, through the sulfur trioxide absorbers *C* and *E*. *C* was packed with glass wool and half-filled with 70% sulfuric acid, and *E* contained soda-lime. The manometer *J* was of the closed tube type, one meter long, and was made from tubing having a bore of 10 mm. A wooden scale with millimeter divisions was used to set the height of the mercury column. The system could be evacuated to 4–5 mm. by a Cenco pump, through stopcock *H*, and filled with air to any desired pressure through stopcock *I*.

The tube leading from the jacket *B* to the by-pass *D*, the by-pass itself, and the tube connecting it to the sulfuric acid chamber *C*, were maintained at about 100° by an electrically heated winding of Chromel wire, to prevent the condensation of

sulfur trioxide. The quartz-to-pyrex joints and the stopcocks F and G were lubricated with a stiff, clear paste made by dissolving phosphorus pentoxide in 85% phosphoric acid at 110°. All other stopcocks were lubricated with a grease made from white vaseline and pure rubber. The general arrangement of the apparatus is best seen from Fig. 2 and the details of the decomposition chamber and water jacket from Fig. 5.

Method of Procedure.—In effecting a controlled decomposition, the sulfate mixture was placed in a porcelain boat p, and anhydrous ferric sulfate placed in another boat q, in the reaction tube, and the latter joined to the Pyrex jacket. After placing the thermocouple in position, stopcock G was opened, F and I closed, and the system evacuated through H. When the pressure had been reduced to 4–5 mm., H and G were closed,

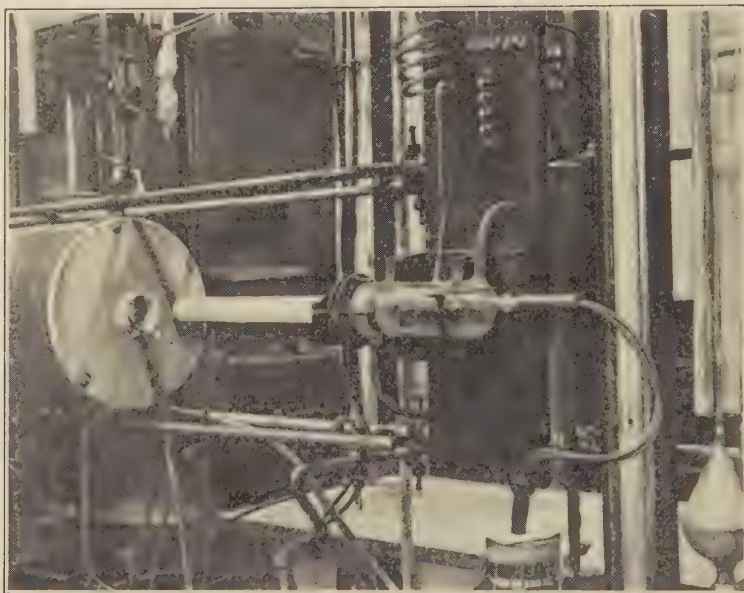


Fig. 5.—Detail of decomposition chamber.

and air admitted through I, to the desired pressure. The ferric sulfate was now decomposed by heating that portion of the quartz tube immediately surrounding it with a blow torch. Stopcock F was opened from time to time to determine when the pressure of sulfur trioxide exceeded the desired value, by noting the direction of movement of the phosphoric acid thread in the by-pass D. As soon as sulfur trioxide started to bubble through the by-pass to the absorbers C and E, stopcock F was left open, and the furnace, which had previously been brought to the desired temperature, moved into such a position over the quartz tube that the decomposition of the ferric sulfate (as well as the sulfates being investigated) proceeded slowly for about three-quarters of an hour. This procedure was found necessary to allow the phosphoric acid in the lubricant, and in the by-pass, to become saturated with sulfur trioxide. After three-quarters of an hour, the furnace was moved completely over the reaction tube, and the reactions allowed to proceed to completion, as indicated by cessation of the bubbling of sulfur trioxide through the by-pass. This required from two to ten hours, depending on the amount of sulfate mixture, and the decomposition temperature.

During the progress of a decomposition it was occasionally necessary to reset the air pressure, since the recombination of the equilibrium mixture of sulfur dioxide and oxygen to sulfur trioxide was not complete, leaving some oxygen which was not taken up by the absorbers C and E.

Upon completion of a decomposition, stopcock F was closed, the furnace moved out of position, and the reaction tube was immediately quenched with cold water, then again evacuated, by opening H and G in succession, and then filled with air by closing H and opening I, after which it was detached from the water jacket, and the boat with the decomposed mixture removed to a desiccator. Due to the thinning out of the phosphoric acid lubricant on the joint between the quartz tube and the water jacket, the two became very firmly stuck together, so that a special screw wedge had to be employed to effect their separation. This may be seen in position in Figure 5. It proved to be very efficacious, and neither the quartz tube nor the water jacket was ever damaged, although at times after the many runs for which they were used, it would have been utterly impossible to get them apart by any other means. No trouble was ever caused by sticking of the very much smaller joint between the thermocouple and the water jacket.

Spectrographic Equipment.—Since none of the rare earths except cerium,¹⁰ europium¹¹ and ytterbium¹² can be determined analytically when present in mixtures with other rare earths, three methods were available for studying the decomposition products of mixed rare earth sulfates: (1) determination of the mean equivalent weight; (2) measurement of the magnetic susceptibility; (3) observation of the emission and absorption spectra.

Of these methods, (1) is of no value when the elements constituting a mixture have atomic weights lying close together; (2) is of value only when the susceptibilities of the elements are considerably different, and (3) can only serve to ascertain with certainty the presence or absence of a particular element in a mixture, although it may afford an approximate idea as to the composition.

The rare earths available for this work were the ceria earths, cerium, neodymium, praseodymium, samarium and lanthanum. As has been mentioned, cerium can be determined analytically. The atomic weights of the other ceria earths are: La, 138.9; Pr, 140.9; Nd, 144.3; and Sm, 150.4. Consequently the determination of the mean equivalent weight of a mixture is of little significance, except possibly in the case of a mixture of samarium with one of the other ceria earths.

The susceptibilities of the ceria earth sulfate octahydrates, expressed in C. G. S. units, are as follows¹³

La	Ce ^{III}	Pr	Nd	Sm
-00.84	+22.0	+51.0	+52.0	+12.0

¹⁰ Willard and Young, *J. Am. Chem. Soc.*, **50**, 1379 (1928); Furman and Wallace, *ibid.*, **51**, 1449 (1929).

¹¹ Yntema, *ibid.*, **52**, 2782 (1930).

¹² Ball and Yntema, *ibid.*, **52**, 4264 (1930).

¹³ Decker, *Ann. Physik*, **79**, 324 (1926).

These values are hardly far enough apart to make the determination of magnetic susceptibility a satisfactory means of analysis.

The comparison of the spectra of the soluble and insoluble products of decomposition with those of the original mixtures was therefore the only reliable means of analysis in studying the decomposition of rare earth sulfate mixtures.

Two spectrographs were available, a small Zeiss glass prism instrument, and a Hilger E-316 quartz spectrograph. The range of the former was 3800 to 8000, and the latter, 2000 to 10,000 Ångström units.

The Zeiss spectrograph was used mainly for absorption spectra in the visible region, with mixtures containing neodymium or praseodymium. The solutions studied were contained in a Baly absorption tube, using a tungsten arc (Point-O-Lite) as a light source.

The arc spectra of the rare earth mixtures were studied with the Hilger spectrograph, using a 6-ampere arc between pure Acheson graphite electrodes.

Quantitative spectrum analysis of rare earth mixtures has been recently described by Quill, Selwood and Hopkins¹⁴ and by Selwood.¹⁵

x-Ray Apparatus.—The crystal structure of the sulfate mixtures was studied by the Hull-Debye-Scherrer powder method of x-ray diffraction, using a General Electric apparatus.¹⁶ Since the method and apparatus involved have been very completely described by Davey,¹⁷ no description is necessary here.

As the diffraction lines obtained by the powder method are rather broad, it was deemed advisable to determine the position of maximum intensity for each line by the use of a Zeiss microphotometer.

Materials.—The sulfates of iron, zinc, beryllium, aluminum, magnesium, nickel and cobalt were of the best quality obtainable from commercial supply houses. The following rare earth salts were kindly supplied by Dr. H. S. Miner of the Welsbach Company: $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$, $\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.

For spectroscopic comparison, the following very pure rare earth oxides were obtained from Adam Hilger, Ltd., London: La_2O_3 , Sm_2O_3 , $\text{PrO}_2 \cdot \text{Pr}_2\text{O}_3$, Nd_2O_3 .

Thermal Decompositions.—Series 1 to 6. Mixtures of non-isomorphous sulfates, and mixtures of cerous sulfate with some other rare-earth

¹⁴ Quill, Selwood and Hopkins, *J. Am. Chem. Soc.*, **50**, 2929 (1928).

¹⁵ Selwood, *Ind. Eng. Chem., Anal. Ed.*, **2**, 93 (1930).

¹⁶ The use of the apparatus was very kindly extended to the authors by Mr. Sherman Gerhard of the Physics Department, to whom appreciation is expressed.

¹⁷ Davey, (a) *J. Optical Soc. Am.*, **5**, 479 (1921); (b) *Gen. Elec. Rev.*, **25**, No. 9, 565 (1922).

sulfates. Anhydrous ferric, aluminum, zinc and beryllium sulfates were prepared from the c. p. hydrated sulfates by heating to constant weight at 400–450°. Anhydrous cerous sulfate was prepared by dehydrating the octahydrate at 600–650°. Anhydrous lanthanum, praseodymium, and neodymium sulfates were prepared from the double ammonium nitrates by evaporation of the latter to dryness with sulfuric acid, and heating of the residues to constant weight at 600–650°. Portions of the anhydrous cerous and lanthanum sulfates were then dissolved separately in cold water, and the cerium oxidized with persulfate in the presence of silver nitrate, according to the method of Willard and Young.¹⁸

After destroying the excess of persulfate by boiling, the ceric sulfate was titrated with freshly standardized hydrogen peroxide according to the method of Furman and Wallace¹⁹ with the following results: $\text{Ce}_2(\text{SO}_4)_3$, 98.49% pure; $\text{La}_2(\text{SO}_4)_3$ contained 1.82% $\text{Ce}_2(\text{SO}_4)_3$. The praseodymium and neodymium sulfates were found to be free from cerium.

Pairs of the anhydrous sulfates were then mixed in the desired proportions, dissolved in 1:5 sulfuric acid, evaporated to dryness and heated to constant weight at 400–450° for those pairs containing iron, zinc, beryllium or aluminum, and at 600–650° for those containing the rare earths. Some of the mixture in each case was then weighed into a small porcelain or quartz boat, which was then placed in a larger boat, and introduced into the decomposition chamber in the manner previously outlined. To prevent the absorption of moisture, weighings were made by placing the crucibles containing the anhydrous sulfates in ordinary weighing bottles, and the boats in specially constructed bottles provided with legs, using a similar empty weighing bottle as a counterpoise.

The reaction tube contained not only the mixed sulfates, but also another boat containing about 10 g. of anhydrous ferric sulfate, and the decomposition was carried out as previously described. The heating was continued until sulfur trioxide ceased to bubble through the phosphoric acid by-pass, and then for one hour more (that is, for six hours unless otherwise noted), after which the sulfates were removed to a desiccator in the manner previously described. After it had been weighed, the decomposed mixture was treated with water, and the insoluble portion filtered off. This was either ignited directly to oxide and weighed, or converted to anhydrous sulfate and then weighed or analyzed, while the soluble portion was either precipitated as hydroxide by sodium carbonate and ignited to oxide and weighed, or else evaporated to dryness, dehydrated, and weighed as anhydrous sulfate. The results are given in Series 1 to 6.

From these results the conclusion was reached that the anhydrous sulfate pairs, Zn-Fe^{III}, Zn-Al, Be-Al, Ce-La, Ce-Pr and Ce-Nd may be sepa-

¹⁸ Willard and Young, *J. Am. Chem. Soc.*, **50**, 1379 (1928).

¹⁹ Furman and Wallace, *ibid.*, **51**, 1449 (1929).

Series 1. $\text{Fe}_2(\text{SO}_4)_3\text{-ZnSO}_4$

Temperature, 800° . Dissociation pressure of $\text{Fe}_2(\text{SO}_4)_3$, >2 atm.
 Pressure, 740 mm. Dissociation pressure of ZnSO_4 , 195 mm.⁴

	Run a, g.	Run b, g.
Composition of mixture $\begin{cases} \text{Fe}_2(\text{SO}_4)_3 \\ \text{ZnSO}_4 \end{cases}$	2.0015 2.3123	1.1250 2.4356
Weight mixture taken	2.3149	2.4356
Weight SO_3 lost	0.6440	0.4616
Theoretical SO_3 loss from $\text{Fe}_2(\text{SO}_4)_3$ forming Fe_2O_3	.6451	.4626
Weight Fe_2O_3 found	.4280	.3068
Weight Fe_2O_3 calculated	.4289	.3075
Weight ZnO found	.6272	.8419
Weight ZnO calculated	.6255	.8405

Series 2. $\text{Al}_2(\text{SO}_4)_3\text{-ZnSO}_4$

Temperature, 800° . Dissociation pressure of $\text{Al}_2(\text{SO}_4)_3$, >2 atm.
 Pressure, 740 mm. Dissociation pressure of ZnSO_4 , 195 mm.⁴

	Run a, g.	Run b, g.
Composition of mixture $\begin{cases} \text{Al}_2(\text{SO}_4)_3 \\ \text{ZnSO}_4 \end{cases}$	2.3146 2.2220	1.2981 2.5673
Weight of mixture taken	2.4563	2.5602
Weight SO_3 lost	0.8788	0.6029
Theoretical SO_3 loss from $\text{Al}_2(\text{SO}_4)_3$ forming Al_2O_3	.8796	.6036
Weight Al_2O_3 found	.3726	.2556
Weight Al_2O_3 calculated	.3733	.2562
Weight ZnO found	.6086	.8588
Weight ZnO calculated	.6065	.8572

Series 3. $\text{BeSO}_4\text{-Al}_2(\text{SO}_4)_3$

Temperature, 750° . Dissociation pressure of BeSO_4 , 365 mm.
 Pressure, 740 mm. Dissociation pressure of $\text{Al}_2(\text{SO}_4)_3$, 900 mm.⁴

	Run a, g.	Run b, g.
Composition of mixture $\begin{cases} \text{BeSO}_4 \\ \text{Al}_2(\text{SO}_4)_3 \end{cases}$	1.5768 1.7632	1.0559 2.3178
Weight of mixture taken	2.5764	2.8377
Actual SO_3 loss	0.9540	1.3675
Theoretical SO_3 loss, from $\text{Al}_2(\text{SO}_4)_3$ forming Al_2O_3	.9548	1.3686
Weight soluble portion as anhydrous sulfate	1.2175	0.8898
Weight BeSO_4 taken	1.2163	.8882
Weight insoluble portion as Al_2O_3	0.4048	.5803
Weight $\text{Al}_2(\text{SO}_4)_3$ found	1.3586	1.9476
Weight $\text{Al}_2(\text{SO}_4)_3$ taken	1.3601	1.9495

Series 4. $\text{Ce}_2(\text{SO}_4)_3\text{-La}_2(\text{SO}_4)_3$

Temperature, 920° . Dissociation pressure of $\text{Ce}_2(\text{SO}_4)_3$, 850 mm.
 Pressure, 740 mm. Dissociation pressure of $\text{La}_2(\text{SO}_4)_3$, 70 mm.⁵

	Run a, g.	Run b, g.
Composition of mixture $\begin{cases} \text{Ce}_2(\text{SO}_4)_3 \\ \text{La}_2(\text{SO}_4)_3 \end{cases}$	1.2134 1.1103	1.3162 0.7263
Weight mixture taken	2.3140	2.0115
Actual $(\text{SO}_2 + \text{SO}_3)$ loss	0.4767	0.5079
Theoretical $(\text{SO}_2 + \text{SO}_3)$ loss	.4771	.5084
Weight of insoluble portion as sulfate	1.2099	1.2890
Weight $\text{Ce}_2(\text{SO}_4)_3$ found by titration in insoluble portion	1.2095	1.2885
Weight $\text{Ce}_2(\text{SO}_4)_3$ taken	1.2102	1.2897

Series 5. $\text{Ce}_2(\text{SO}_4)_3$ - $\text{Pr}_2(\text{SO}_4)_3$

Temperature, 920° . Dissociation pressure of $\text{Pr}_2(\text{SO}_4)_3$, 145 mm.⁵
 Pressure, 740 mm.

	Run a, g.	Run b, g.
Composition of mixture $\left\{ \begin{array}{l} \text{Ce}_2(\text{SO}_4)_3 \\ \text{Pr}_2(\text{SO}_4)_3 \end{array} \right.$	0.5326 .5116	0.7896 .4317
Weight mixture taken	1.0237	1.1987
Actual ($\text{SO}_2 + \text{SO}_3$) loss	0.2025	0.3004
Theoretical ($\text{SO}_2 + \text{SO}_3$) loss	.2027	.3009
Weight of insoluble portion as sulfate	.5139	.7627
Weight $\text{Ce}_2(\text{SO}_4)_3$ found by titration in insoluble portion	.5139	.7624
Weight $\text{Ce}_2(\text{SO}_4)_3$ taken	.5143	.7633

Series 6. $\text{Ce}_2(\text{SO}_4)_3$ - $\text{Nd}_2(\text{SO}_4)_3$

Temperature, 920° . Dissociation pressure of $\text{Nd}_2(\text{SO}_4)_3$, 170 mm.⁵
 Pressure, 740 mm.

	Run a, g.	Run b, g.
Composition of mixture $\left\{ \begin{array}{l} \text{Ce}_2(\text{SO}_4)_3 \\ \text{Nd}_2(\text{SO}_4)_3 \end{array} \right.$	0.5116 .4998	0.6321 .3872
Weight mixture taken	.9992	.9976
Actual ($\text{SO}_2 + \text{SO}_3$) loss	.1958	.2395
Theoretical ($\text{SO}_2 + \text{SO}_3$) loss	.1962	.2402
Weight of insoluble portion as sulfate	.4972	.6087
Weight $\text{Ce}_2(\text{SO}_4)_3$ found by titration in insoluble portion	.4969	.6082
Weight $\text{Ce}_2(\text{SO}_4)_3$ taken	.4978	.6093

rated into their constituents by controlled decomposition. The first three pairs are made up of non-isomorphous sulfates; solid solutions do not ap-

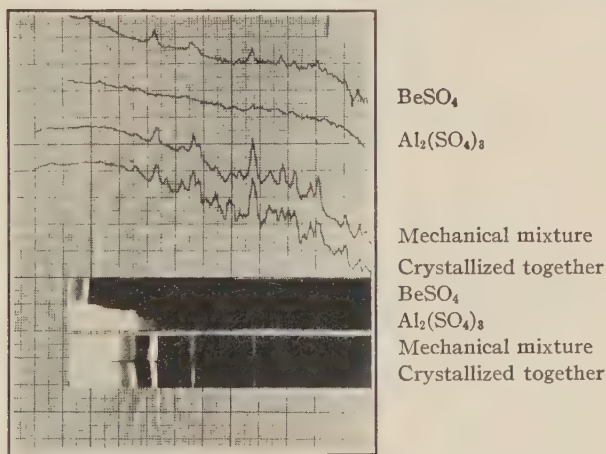


Fig. 6.—x-Ray spectra and photometer curves of beryllium and aluminum sulfates.

pear to be formed in these cases. x-Ray diffraction photographs taken by the Hull-Debye-Scherrer method on the Be-Al sulfate mixture confirm these conclusions, no evidence of solid solution formation being shown, as the lines occurring in the individual spectra of the pure sulfates appear

without shift in the spectra of the mixture. This is evident from Fig. 6, particularly from the photometer curves.

Cerous sulfate is isomorphous with the other rare earth sulfates, but thermal decomposition results in CeO_2 , which is not isomorphous with the rare earth sesquioxides; as the results show, separation of cerium from the other rare earths by controlled thermal decomposition is therefore possible.

Series 7 to 12. Mixtures of isomorphous sulfates, including some rare earth sulfate mixtures not containing cerium. Anhydrous sulfates of nickel, cobalt and magnesium were prepared from the c. p. hydrated sulfates by heating to constant weight at 500–650°, the lower temperature being necessary for nickel. Pairs of these and pairs of the anhydrous sulfates of lanthanum, praseodymium and neodymium were then mixed, dissolved in water, dehydrated and decomposed in a manner exactly analogous to that of Series 1 to 6. In addition to the mixed sulfates, the pure sulfate constituents of each pair were placed simultaneously in the decomposition chamber, in separate adjacent boats. The results are shown in Series 7 to 12.

Series 7. BeSO_4 – ZnSO_4 .—Temperature, 800°. Pressure, 740 mm. Dissociation pressure of BeSO_4 , 950 mm.; of ZnSO_4 , 195 mm. 2.0132 g. of pure BeSO_4 lost 1.2263 g. of SO_3 , forming $5\text{BeO} \cdot \text{SO}_3$; theoretical loss, 1.2272 g. The residue was boiled for thirty minutes with water. After filtering off the residue, ammonia produced in the filtrate only a slight turbidity, indicating complete decomposition of the BeSO_4 . 2.3216 g. of pure ZnSO_4 lost 0.0013 g.; theoretically there should have been no loss. Hot water dissolved all but a trace of it.

The mixture consisted of 2.6512 g. of ZnSO_4 and 2.1314 g. of BeSO_4 . Of this mixture, 2.1206 g. lost 0.6561 g. of SO_3 as compared to a theoretical of 0.5760 if only BeSO_4 decomposed. The weight of the insoluble portion, converted into anhydrous sulfates, was 1.2828 g. The beryllium in this was precipitated as $\text{Be}(\text{OH})_2$ by ammonia and yielded 0.1649 g. of BeO , corresponding to 0.6925 g. of BeSO_4 and leaving 0.5903 g. of ZnSO_4 . The original mixture contained 44.57% of BeSO_4 and the decomposed portion, 53.98%.

Series 8. BeSO_4 – MgSO_4 .—Temperature, 1000°. Pressure, 740 mm. Dissociation pressure of $\text{BeSO}_4 > 2$ atm.; of MgSO_4 , 60 mm.⁴ 2.5316 g. of pure BeSO_4 lost 1.5432 g. of SO_3 , forming $5\text{BeO} \cdot \text{SO}_3$; theoretical loss 1.5430 g. The residue was tested as above with the same results. 3.1579 g. of pure MgSO_4 lost 0.0003 g., or practically no loss, and hot water dissolved all but a trace of it.

The mixture consisted of 1.5632 g. of BeSO_4 and 1.5226 g. of MgSO_4 . Of this, 2.5350 g. lost 0.7685 g. of SO_3 instead of the theoretical 0.7827 g. The insoluble portion as anhydrous sulfates weighed 1.3345 g. and contained 0.7551 g. of BeSO_4 , leaving 0.5794 g. of MgSO_4 . The original mixture contained 50.66% of BeSO_4 and the decomposed portion, 56.58%.

Series 9. NiSO_4 – CoSO_4 .—Temperature, 920°. Pressure, 740 mm. Dissociation pressure of NiSO_4 , 1400 mm.; of CoSO_4 , 420 mm.⁴ 2.6882 g. of NiSO_4 lost 1.3910 g. of SO_3 , instead of the theoretical 1.3908, g. to form NiO . It was completely insoluble in water. 3.7645 g. of CoSO_4 lost 0.0003 g. or practically nothing, and all but a trace of it was soluble in water.

The mixture consisted of 2.5031 g. of NiSO_4 and 2.6345 g. of CoSO_4 . Of this, 2.7543 g. lost 0.8290 g. instead of the theoretical 0.6943 g. The residue was extracted with hot water, and the insoluble portion, treated with sulfuric acid and heated to con-

stant weight at 500–550° yielded 1.6022 g. of anhydrous sulfates. The nickel in this was determined by double precipitation with dimethylglyoxime. The cobalt was determined by difference. The same method was used for the soluble portion. In the insoluble portion, weighing, as sulfates, 1.6022 g., the weight of NiSO_4 was 1.0193 g. and the CoSO_4 , 0.5829 g. The soluble portion, by difference, amounted to 1.1521 g. and consisted of 0.3226 g. of NiSO_4 and 0.8295 g. of CoSO_4 . Thus the NiSO_4 constituted 48.72% of the original mixture, 62.17% of the insoluble residue and 28.00% of the soluble portion.

The x-ray diffraction photographs and their photometer curves in Fig. 7 show very clearly evidence of formation of solid solutions. There is a distinct shift of the lines in the crystallized mixture as compared with those for the pure substances or in a mechanical mixture.

Series 10. $\text{Nd}_2(\text{SO}_4)_3$ – $\text{La}_2(\text{SO}_4)_3$.—Temperature, 1020°. Pressure 740 mm. Dissociation pressure of $\text{Nd}_2(\text{SO}_4)_3$, 840 mm.; of $\text{La}_2(\text{SO}_4)_3$, 370 mm. In run A, 0.5982 g. of pure $\text{Nd}_2(\text{SO}_4)_3$ lost 0.1650 g. of SO_3 , forming $\text{Nd}_2\text{O}_3 \cdot \text{SO}_3$; theoretical loss, 0.1660 g. Only a few tenths of a mg. dissolved in water. 0.6147 g. of pure $\text{La}_2(\text{SO}_4)_3$ lost 0.0047 g., due to the impurity of $\text{Ce}_2(\text{SO}_4)_3$, which should have lost 0.0044 g.; all but a trace dissolved.

The mixture consisted of 0.4322 g. of $\text{Nd}_2(\text{SO}_4)_3$ and 0.4418 g. of $\text{La}_2(\text{SO}_4)_3$. 0.8613 g. of this lost 0.0479 g. instead of the theoretical 0.1213 g. The decomposed mixture was then treated with water. The undecomposed portion of the mixture was dissolved, the residue filtered off, converted to anhydrous sulfate by evaporation with concentrated sulfuric acid and heated at 600° to constant weight. This resulted in 0.1722 g. of anhydrous sulfate mixture.

The approximate composition of the decomposed portion of the sulfate mixture was calculated from its weight and the total loss of sulfur trioxide as being 0.155 g. $\text{Nd}_2(\text{SO}_4)_3$, 0.017 g. $\text{La}_2(\text{SO}_4)_3$.

A qualitative confirmation of the fractionation was obtained by photographing the arc spectra of the soluble and insoluble portions. It is evident that the apparent fractionation of the neodymium-lanthanum sulfate

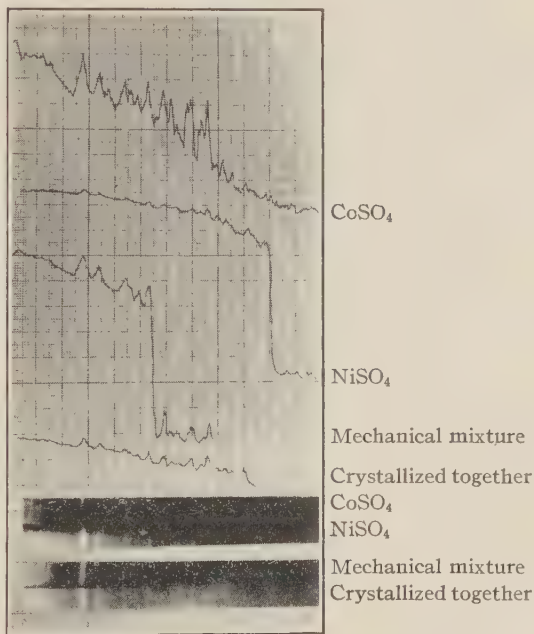


Fig. 7.—x-Ray spectra and photometer curves of cobalt and nickel sulfates.

mixture is due only to the fractionation obtained in crystallization; that is, all crystals deposited previous to a certain point in the process of crystallization will have such a composition that their decomposition pressures will be less than the pressure of sulfur trioxide arbitrarily maintained in the reaction chamber, while all those subsequently deposited will be sufficiently rich in neodymium sulfate so that their decomposition pressures will exceed this pressure.

Run (B).—To confirm the conclusions drawn from Run (A) the following experiment was performed.

The two fractions obtained in Run (A) were dissolved together in water, and the solution placed in a 100-cc. graduated cylinder, which was then immersed in a beaker of oil, on a hot-plate. When crystals just started to appear, the volume of the solution was noted, and the evaporation continued until the volume had decreased to one-fifth of the value noted. The remaining solution was then quickly decanted from the crystals (which we may designate A) into a small beaker, and the evaporation continued in this, to dryness, resulting in a second portion of crystals, B. Crystals A with adhering solution were transferred to a small beaker, and evaporated to dryness. The two crystalline masses were then heated to constant weight at 600°, and placed in separate adjacent boats in the reaction chamber. The pressure of sulfur trioxide and the temperature were set to the values used in Run (A). After four hours' heating, the boats were removed from the furnace, cooled, and their contents treated with water. Practically all of the crystals A dissolved, while only a very small part of the crystals B went into solution. The arc spectra of A and B showed B to be richer in neodymium than A.

Series 11. $\text{Pr}_2(\text{SO}_4)_3$ – $\text{La}_2(\text{SO}_4)_3$.—Temperature, 1030°. Pressure, 740 mm. Dissociation pressure of $\text{Pr}_2(\text{SO}_4)_3$, 865 mm.; of $\text{La}_2(\text{SO}_4)_3$, 430 mm. 0.5774 g. of pure $\text{Pr}_2(\text{SO}_4)_3$ lost 0.1615 g. of SO_3 , forming $\text{Pr}_2\text{O}_3\cdot\text{SO}_3$; theoretical loss, 0.1622. It was practically insoluble in water. 0.6744 g. of pure $\text{La}_2(\text{SO}_4)_3$ lost 0.0050 g. due to the impurity of $\text{Ce}_2(\text{SO}_4)_3$, which required 0.0048 g. All but a very small amount dissolved in water.

The mixture consisted of 0.3216 g. of $\text{Pr}_2(\text{SO}_4)_3$ and 0.3114 g. of $\text{La}_2(\text{SO}_4)_3$. Of this mixture, 0.6312 g. lost 0.0344 g. of SO_3 , instead of the theoretical 0.0923 g. The insoluble portion was filtered off and converted into anhydrous sulfates weighing 0.1222 g. From this weight and the loss in SO_3 the composition of the insoluble portion was calculated to be 0.106 g. of $\text{Pr}_2(\text{SO}_4)_3$ and 0.016 g. of $\text{La}_2(\text{SO}_4)_3$.

Series 12. $\text{Nd}_2(\text{SO}_4)_3$ – $\text{Pr}_2(\text{SO}_4)_3$.—Temperature, 1015°. Pressure, 740 mm. Dissociation pressure of $\text{Nd}_2(\text{SO}_4)_3$, 780 mm.; of $\text{Pr}_2(\text{SO}_4)_3$, 715 mm. 0.5549 g. of pure $\text{Nd}_2(\text{SO}_4)_3$ lost 0.1553 g. of SO_3 , forming $\text{Nd}_2\text{O}_3\cdot\text{SO}_3$; theoretical loss, 0.1562 g. It was practically insoluble in water. 0.6117 g. of $\text{Pr}_2(\text{SO}_4)_3$ lost 0.0003 g. or practically nothing; all but a trace dissolved in water.

The mixture consisted of 0.3227 g. of $\text{Nd}_2(\text{SO}_4)_3$ and 0.3009 g. of $\text{Pr}_2(\text{SO}_4)_3$. Of this, 0.6125 g. lost 0.0041 g., instead of the theoretical 0.0892 g., and all but about 0.01 g. dissolved in water.

Series 13. BeSO_4 – K_2SO_4 .—The double sulfate $\text{BeSO}_4\cdot\text{K}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ was prepared by dissolving equimolar quantities of BeSO_4 and K_2SO_4 , together in water, and crystallizing by slow evaporation in a vacuum desiccator containing sulfuric acid. The double salt separated in the form of fine crystals. These were then dehydrated at 400°, a portion of the anhydrous material dissolved in water, and the beryllium determined by precipitation as hydroxide with ammonia, and ignition to BeO . The results were as follows.

Weight of $\text{BeSO}_4\cdot\text{K}_2\text{SO}_4$, g.	2.5842
Weight of BeO found, g.	0.2319
Ratio $\text{BeSO}_4/\text{K}_2\text{SO}_4$ calculated	1.0021

A weighed portion of the anhydrous double sulfate, in a boat provided with a platinum cover (to avoid possible loss by spattering, because the double sulfate melts at 900°), was then placed in the reaction tube, and heated for six hours at 930°, the pressure of sulfur trioxide being set to 740 mm. The dissociation pressure of the double sulfate is given by Mlle. Marchal⁴ as 806 mm., at 930°. The dissociation pressure of

potassium sulfate at this temperature is undoubtedly very much less than 740 mm. After cooling and removing from the furnace, the boat was weighed, with the following result

Weight of $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4$, g.	2.2177
Theoretical SO_3 loss, from BeSO_4 forming BeO , g.	0.6346
Actual SO_3 loss, g.	.6339

The contents of the boat were then treated with hot water, the insoluble BeO filtered off on a Gooch crucible and ignited to constant weight, with the following result

Weight BeO found, g.	0.1978
Weight BeO calculated, g.	.1986

This experiment shows that the controlled decomposition of $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4$ results in the formation of BeO and K_2SO_4 . At 930° the dissociation pressure of the basic $5\text{BeO} \cdot \text{SO}_3$ is apparently greater than 840 mm., as there was no indication of its formation.

Series 14. PrO_2 - La_2O_3 Mixture.—It is evident from the behavior of all the mixtures of isomorphous sulfates, except those containing cerous sulfate, that the formation of solid solutions prevents the constituent sulfates from exerting their individual dissociation pressures and that the separation of the constituents is therefore impossible. The fact that cerous sulfate can be made to decompose preferentially in mixtures with others of the isomorphous rare earth sulfates is explainable as follows.

The dissociation pressure of a mixture of cerous, and, say, lanthanum sulfate, has some value intermediate between the dissociation pressures of pure $\text{Ce}_2(\text{SO}_4)_3$ and pure $\text{La}_2(\text{SO}_4)_3$, the precise value being dependent upon the composition of the mixture. If now the pressure of sulfur trioxide in the decomposition apparatus be set just above the dissociation pressure of pure $\text{La}_2(\text{SO}_4)_3$ at the temperature used, all the crystals will decompose into a mixture of CeO_2 and La_2O_3 because of the very great instability of $\text{Ce}_2\text{O}_3 \cdot \text{SO}_3$. Since CeO_2 and La_2O_3 (or any other rare earth sesquioxide) have crystal structures of quite different types,²⁰ the decomposition will thus have resulted in the breaking up of the solid solution, so that the mixture will consist of individual crystals of CeO_2 and La_2O_3 . The SO_3 pressure in the apparatus being greater than the dissociation pressure of $\text{La}_2(\text{SO}_4)_3$, the La_2O_3 will recombine with SO_3 to form the normal sulfate, and a separation will have been effected.

The normal oxide in the rare earths is the sesquioxide. However, in addition to the known stable CeO_2 , there is evidence of dioxide formation in the cases of praseodymium²¹ and terbium.²⁰ In the case of praseodymium, it is impossible to obtain the sesquioxide by heating the nitrate, carbonate or oxalate, higher oxides approximating the composition PrO_2

²⁰ Goldschmidt, Ulrich and Barth, *Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo, I. Matem. Naturvid. Klasse*, No. 5, pp. 5-24 (1925), *Chemical Abstracts*, 19, 2764 (1925).

²¹ Pagel and Brinton, *J. Am. Chem. Soc.*, 51, 42 (1929).

being obtained. In order to get the sesquioxide, these higher oxides must be reduced by hydrogen at 600–800°.

It is evident that in order to obtain a separation by controlled sulfate decomposition, the solid solution of two isomorphous sulfates must be broken up. From Series 11, it is seen that such a break-up does not occur on heating a mixture of praseodymium and lanthanum sulfates, the $\text{Pr}_2\text{O}_3 \cdot \text{SO}_3$ being a stable substance, in contradistinction to the cerous basic sulfate. Now since the heating of a mixture of the nitrates of praseodymium and lanthanum results in the formation of PrO_2 (at least in part) and La_2O_3 , and since PrO_2 has a crystal structure similar to that of CeO_2 , breaking up of the solid solution of $\text{Pr}(\text{NO}_3)_3$ and $\text{La}(\text{NO}_3)_3$ would be the result. The crystals of PrO_2 and La_2O_3 would still have to be separated, however, which would be very difficult. But if the mixed oxides were placed in the controlled decomposition apparatus, and the temperature set to some definite value, with sulfur trioxide provided from the decomposition of ferric sulfate, at a pressure less than that of pure $\text{Pr}_2(\text{SO}_4)_3$, but greater than that of $\text{La}_2(\text{SO}_4)_3$, the PrO_2 should form $\text{Pr}_2\text{O}_3 \cdot \text{SO}_3$, while the La_2O_3 should form $\text{La}_2(\text{SO}_4)_3$. Separation by solution of the latter would then be possible. The separation cannot be complete because some Pr_2O_3 will always be present. An experiment to test these considerations was therefore performed in the following manner.

About 0.3 g. each of anhydrous $\text{Pr}_2(\text{SO}_4)_3$ and $\text{La}_2(\text{SO}_4)_3$ were dissolved together in water, and oxalic acid added in slight excess, to precipitate the mixed oxalates. These were filtered off, and ignited to oxides. The oxides were dissolved in concentrated nitric acid, the solution evaporated down to small volume, transferred to a platinum crucible, and the evaporation continued to dryness. The crucible was then heated over a Méker burner until the evolution of the oxides of nitrogen ceased, after which it was placed in an electric muffle and heated at 400–450° for three hours. After cooling, the greater portion of the dark brown mixture of PrO_2 – Pr_2O_3 and La_2O_3 was transferred to a boat and placed in the reaction tube. This boat was followed as in all the other runs, by another boat containing anhydrous ferric sulfate. The furnace, which had been previously set to maintain a temperature of 1010°, was then brought into position over the reaction tube, at such a rate that the evolution of sulfur trioxide from the ferric sulfate was just fast enough for the mixed oxides to absorb it, only a bubble or two per second escaping through the phosphoric acid by-pass into the absorption chambers, wherein the air pressure had been set to a pressure of 740 mm. At 1010° the dissociation pressures of $\text{Pr}_2(\text{SO}_4)_3$ and $\text{La}_2(\text{SO}_4)_3$ are 660 and 317 mm., respectively. When all the ferric sulfate had decomposed and no more sulfur trioxide escaped through the by-pass, the furnace was removed from over the reaction chamber, and the boat, the contents of which were now green in color, removed to a desiccator to cool, and then weighed. The boat was then again placed in the reaction tube, with a fresh charge of ferric sulfate, and the procedure described above repeated to make certain the complete conversion of the oxides to sulfates. A second weighing showed practically no change, so it was assumed that such was the case. It is interesting to note that the combination of the oxides with sulfur trioxide was quite rapid, it being necessary to subject them to its action for only about forty-five minutes for complete conversion to sulfates. This shows that the dissociation of the sulfates is readily reversible, and indicates the necessity for

very rapid cooling after the removal of the furnace from the reaction tube, to "quench" the high-temperature equilibrium.

After the second weighing the boat was once more put into the decomposition chamber, and the mixed sulfates decomposed in the same manner as in all the other runs, the temperature and pressure being set at 1030° and 740 mm., respectively. Four hours' time was allowed for the completion of the decomposition, after which the boat was removed to a desiccator to cool, then weighed, with the results given.

Composition of mixture, g. $\left\{ \begin{array}{l} \text{Pr}_2(\text{SO}_4)_3 \\ \text{La}_2(\text{SO}_4)_3 \end{array} \right.$	0.3019
	.3105
Weight of sulfates converted from oxides, g.	.5176
SO_3 loss from these sulfates, after subtracting loss from $\text{Ce}_2(\text{SO}_4)_3$ impurity, g.	.0718
Theoretical SO_3 loss, from $\text{Pr}_2(\text{SO}_4)_3$ forming $\text{Pr}_2\text{O}_3 \cdot \text{SO}_3$, g.	.0716

The contents of the boat were then treated with cold water. A portion dissolved, resulting in a practically colorless solution; the insoluble portion, which was quite green in color, was filtered off, treated with concentrated sulfuric acid, evaporated to dryness, and heated to constant weight at 600° . This resulted in 0.2558 g. of anhydrous $\text{Pr}_2(\text{SO}_4)_3$ and $\text{La}_2(\text{SO}_4)_3$. From this weight and the loss of sulfur trioxide, 0.235 g. of $\text{Pr}_2(\text{SO}_4)_3$ and 0.021 g. of $\text{La}_2(\text{SO}_4)_3$ were calculated to have decomposed.

That the greater part of the praseodymium had been concentrated into the insoluble portion was further indicated by a comparison of the absorption spectrum of this portion with that of the soluble portion. The former showed the bands of praseodymium quite distinctly, the latter only very faintly, when an approximately 5% solution of each, 10 cm. in thickness, was interposed between the Point-O-Lite and spectrograph. A further confirmation was obtained by comparing the arc spectrum of each portion with the spectrum of the original mixture.

These results show that at least a partial separation of lanthanum and praseodymium can be made if a solid solution of their isomorphous salts be broken up into two solid phases, by the

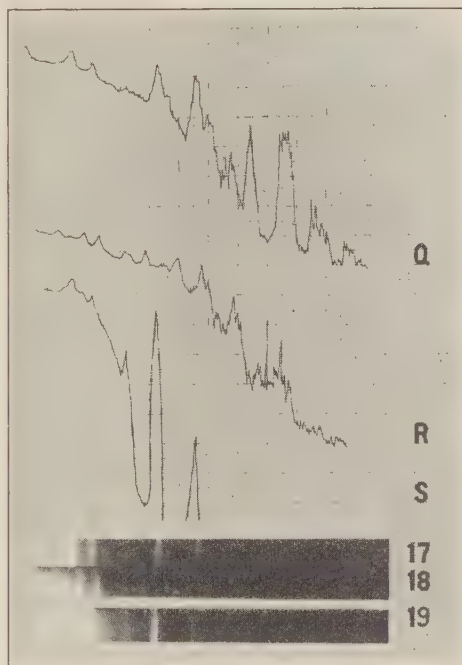


Fig. 8.—x-Ray diffraction by La_2O_3 , $\text{PrO}_2\text{-Pr}_2\text{O}_3$, and a mixture of La_2O_3 and $\text{PrO}_2\text{-Pr}_2\text{O}_3$.

process of converting them to La_2O_3 and PrO_2 and then to $\text{La}_2(\text{SO}_4)_3$ and $\text{Pr}_2\text{O}_3 \cdot \text{SO}_3$.

x-Ray Study of the PrO_2 - La_2O_3 Mixture.—A Hull-Debye-Scherrer powder tube (Reference 17a, page 487) was filled with some of the brown mixture of PrO_2 , Pr_2O_3 and La_2O_3 obtained in the experiments of Series 14. This tube was then placed in a cassette on the x-ray apparatus, and exposed to the K radiation from a molybdenum target Coolidge tube for twenty-four hours, using a filament current of 25 milliamperes. Another powder tube was half filled with some of the pure black PrO_2 - Pr_2O_3 mixture obtained from Hilger, and half with pure La_2O_3 from the same source; an exposure of the same time and with the same filament current was then made.

The diffraction lines and their photometer curves are shown by Fig. 8, in which 17 and Q are from pure PrO_2 - Pr_2O_3 , 18 and R from pure La_2O_3 and 19 and S from the brown mixture of PrO_2 and La_2O_3 . These x-ray photographs show very clearly that PrO_2 has a crystal structure decidedly different from that of La_2O_3 , and that both PrO_2 and La_2O_3 crystals result from the thermal decomposition of the mixed nitrates and therefore confirm the conclusions drawn from the experiments of Series 14.

Summary

1. The design and construction of a low-voltage electric high-temperature furnace using heating coils made of chromel wire and a photo-electrically operated thermostat capable of maintaining the furnace to within 0.1° of any desired temperature between 700 and 1100° have been described.

2. An all-glass-and-quartz apparatus for studying the decomposition of sulfates at high temperatures and at constant pressures of sulfur trioxide has been described.

3. The thermal decomposition of various binary mixtures of anhydrous sulfates formed by evaporation of mixed solutions has been studied. It has been found that mixtures of the non-isomorphous sulfates of ferric iron and zinc, aluminum and zinc, and beryllium and aluminum, may be preferentially decomposed so that the sulfate having the greatest dissociation pressure at a given temperature will be converted into an insoluble basic sulfate, or oxide, thus permitting a ready separation from the unchanged sulfate by solution of the latter in water.

4. Anhydrous mixed crystals of the isomorphous sulfates of nickel and cobalt, beryllium and zinc, beryllium and magnesium, lanthanum and praseodymium and neodymium and praseodymium were found to decompose into mixed crystals of basic sulfates or oxides, a separation being, therefore, impossible. The mixed crystals behave as a single phase, possessing a definite dissociation pressure at a given temperature, this

pressure being intermediate between the dissociation pressures of the pure constituent sulfates and dependent on their relative amounts.

5. Cerous sulfate, in anhydrous mixtures with the isomorphous sulfates of lanthanum, praseodymium and neodymium, was found to be preferentially decomposable into CeO_2 , as a consequence of the different crystal lattices of CeO_2 and the rare-earth sesquioxides.

6. The mixed nitrates of praseodymium and lanthanum decompose at $400\text{--}450^\circ$ into the two solid phases PrO_2 and $\text{La}_2\text{O}_3\text{--Pr}_2\text{O}_3$; these oxides may then be converted into $\text{Pr}_2\text{O}_3\cdot\text{SO}_3$ and $\text{La}_2(\text{SO}_4)_3\text{--Pr}_2(\text{SO}_4)_3$ and a considerable separation effected by solution of the latter in water.

7. x-Ray diffraction photographs of some mixtures of oxides and of anhydrous sulfates, obtained by the Hull-Debye-Scherrer powder method, confirmed the conclusions drawn from the decomposition experiments, as to the formation of solid solutions.

